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Letter

Loss of ferromagnetism in $PrYSi_{3-\delta}$

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Abstract

The magnetic properties of the compound $Pr_2Si_{3-\delta}$ are governed by two sublattices, each having a separate ordering temperature and sublattice moment. The substitution of yttrium proceeds by means of a preferential occupation by yttrium of the site with the higher moment and Curie temperature and leads to a breakdown of ferromagnetism.

In a previous investigation we reported on the crystallographic and magnetic structure of the silicon-deficient compound $Pr_2Si_{3-\delta}$ [1]. We showed that this compound is characterized by two praseodymium sites and that both corresponding praseodymium sublattices give rise to ferromagnetic ordering, but do so at different temperatures. The silicon deficiency is restricted to only one of the three silicon positions and affects primarily the Pr(1) atoms, for which about half of the 12 nearest-neighbour silicon positions are 72% occupied. We suggested that it is primarily the random crystal field experienced by the Pr(1) atoms that leads to low praseodymium moments (1.8 μ_B) and low ordering temperature ($T_{c1} = 40$ K). The praseodymium moments and ordering temperature associated with the Pr(2) site are much higher (3.1 μ_B and $T_{c2} = 100$ K). Given these differences in silicon coordination, it appeared reasonable to assume that substitutions of yttrium for praseodymium will lead to a strong preference of yttrium for one of the two rare earth sites. In this letter we will show that this is indeed the case. The yttrium substitutes almost primarily into the Pr(2) sites, with the consequence that ferromagnetism completely breaks down even for temperatures far below T_{c1}.

A sample of composition $PrYSi_{2.66}$ was prepared by arc melting the elements in an atmosphere of purified argon gas. The purity of the starting

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materials was 99.9% for yttrium and praseodymium and 99.99% for silicon. The arc-cast sample was vacuum annealed at 1100 °C for 3 weeks and subsequently quenched in water. After annealing, the sample was powdered and examined by standard X-ray diffraction, which showed that it was approximately single phase.

Neutron diffraction was performed on powdered material at various temperatures in the paramagnetic state as well as in the magnetically ordered state with the "DMC" (Double Axis Multicounter System) at the Reactor Saphir, Wuerenlingen, $\lambda = 1.7012$ Å, using the high intensity mode [2]. The step increment of the diffraction angle 2θ was 0.10°. The data were corrected for absorption and for impurity contributions evaluated by the multipattern Rietveld programme [3, 4], using scattering lengths for praseodymium, yttrium and silicon as reported in ref. 5.

The data collected in the paramagnetic state (at 140 K) indicate the presence of foreign phases of FeB and AlB_2 type as in the pure praseodymium compound. This fact complicates matters in so far that we have to assume that yttrium replaces praseodymium also in the impurity phase, which necessitates the adaptation of the corresponding parameters. In order to determine the Pr:Y distribution in the main phase, we first carried out model calculations for three cases in which yttrium occupies the two available rare earth sites at random (model I) or in which yttrium occupies one of these two sites preferentially (models II and III). The silicon occupancy for all three cases was taken as 72% for the Si(1) position. From a comparison of the results with experiment we found that model III, in which yttrium occupies the R(2) position, is closest to the observations.

The results were used in the refinement of the 9 K data shown in Fig. 1, which were collected with a counting rate twice that of the 140 K data. The refinement is a further confirmation of the preferred R(2) site occupation of the Y atoms, since it shows that only 8% of the Y atoms are at position R(1). The occupancy factors of Y atoms in the R sites of the FeB and AlB_2 types were fixed in this refinement procedure at 50%. The reliability factors of the refinement are not as satisfactory as those found for the pure compound $Pr_2Si_{3-\delta}$ owing to the weavy nature of the background. This is probably due to the fact that atoms at the same site have different scattering lengths and due to the presence of other secondary phases in this ternary system. Nevertheless, the refinement reveals that the Si(1) sites are only partly occupied, the occupation factor being the same as in pure $Pr_2Si_{3-\delta}$.

The difference diagram 9–60 K shown in Fig. 2 indicates that at the positions of the reflections 020, 110, 170 and 131, where the main magnetic contributions of the Pr(1) site would be expected, there is hardly any extra intensity distinguishable from the background. This indicates that at about 9 K the ordered moment value of Pr(1) must be absent or at least be less than 0.4 μ_B (Table 1). Substitution of yttrium for Pr(2) has completely destroyed the magnetic ordering of this position, characterized by the largest praseodymium moment and a fully occupied silicon polyhedron around it. Apparently, magnetic interaction between the Pr atoms at the R(1) position,

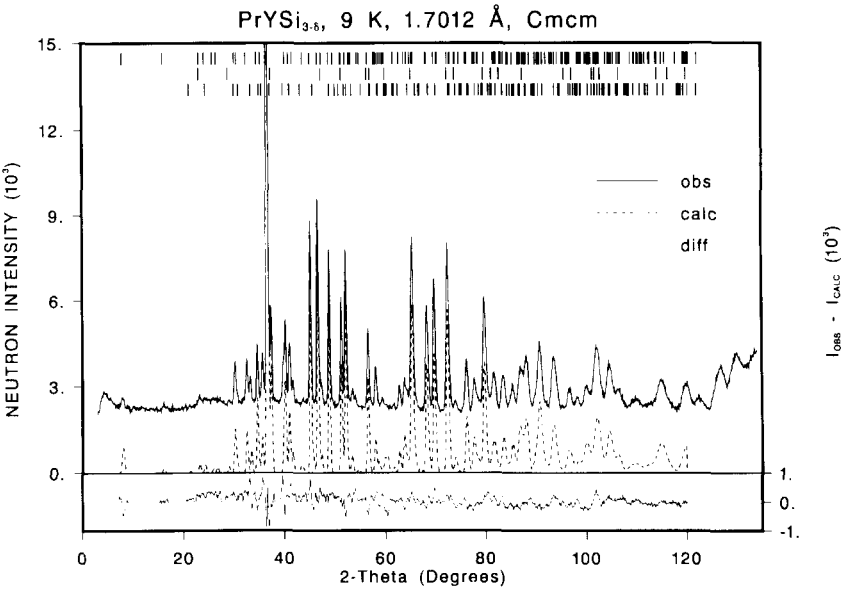

Fig. 1. Observed (solid line) and calculated (broken line) neutron diffraction patterns of the compound of nominal composition $PrYSi_{2.66}$ measured at 9 K. The diffraction pattern consists of a mixture of lines of the defect compounds $PrYSi_{3-\delta}$, low intensity contributions due to $(PrY)Si_{1.8}$ (AlB_2-type) and contributions due to (Pr,Y)Si (FeB type). All sets of lines were refined simultaneously.

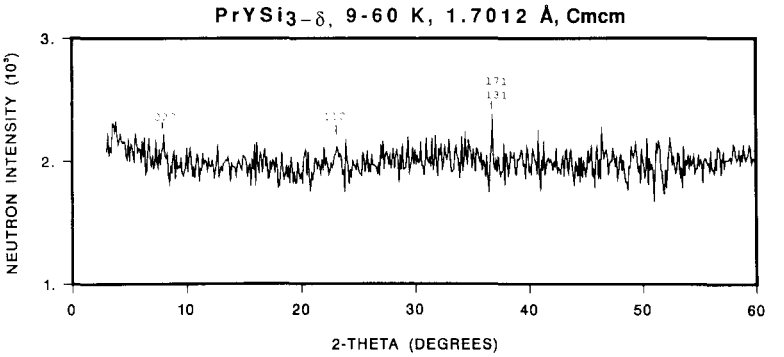

Fig. 2. Difference neutron diagram obtained by subtraction of the contributions of the paramagnetic state at 60 K from the diffraction pattern measured at 9 K.

if it exists, must be very small and the corresponding ordering temperature would lie below 9 K. Although the previous observation [1] of two distinct, well-separated magnetic ordering temperatures for the Pr(1) and Pr(2) sublattices in $Pr_2Si_{3-\delta}$ had suggested that the coupling between these two sublattices is fairly weak, the present results show that the Pr(1) sublattice alone is not able to generate the ordering temperature $T_{c1} = 40$ K. We conclude, therefore, that the exchange fields produced by the Pr(2) sublattice are crucial for the ferromagnetism of the Pr(1) sublattice.

TABLE 1

Refined parameters from the 9 K neutron data of the $PrYSi_{3-\delta}$ compound. The refinement suggests the composition $RSi_{1.36}$. All atoms occupy the 4*c* symmetry position. The rare earth site R(2) is 92% occupied by yttrium

Atom	*x*	*y*	*z*
R(1)	0.0	0.4276(4)	0.25
R(2)	0.5	0.2006(2)	0.25
Si(1)[a]	0.0	0.0168(6)	0.25
Si(2)	0.0	0.1134(4)	0.25
Si(3)	0.5	0.3263(4)	0.25
$B_{Pr,Y}$ (nm^2)	0.0082(7)		
B_{Si} (nm^2)	0.012(1)		
μ_z (μ_B)	<0.4(1)		
a (nm)	0.43025(4)		
b (nm)	2.4319(30)		
c (nm)	0.38752(4)		
R_n, R_m, R_{wp} (%)	13.8, –, 16.0		
R_{exp} (%), χ^2	5.6, 8.1		

[a]This position is only 72% occupied.

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Note added in proof

Recent neutron investigations confirm the loss of ferromagnetism down to 1.5 K.